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TITLE: THIN SOLID FILMS: An International Journal on the Science and Technology of Condensed Matter Films. Volume 412 Nos. 1-2, June 3, 2002. Proceedings of the Workshop on MBE and VPE Growth, Physics, Technology [4th], Held in Warsaw, Poland, on 24-28 September 2001

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Polarity selection process and polarity manipulation of GaN in MOVPE and RF-MBE growth

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Abstract

The polarity-controlled growth of GaN on a sapphire substrate by metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) was demonstrated. The mechanisms for polarity reversion of GaN by TMAI preflow in MOVPE growth and high-temperature deposited AlN intermediate layers in MBE growth were discussed based on the ‘two monolayers of Al’ model. The kinetic process of GaN polarity selection on a sapphire substrate, Al layers, and AlN surface was investigated by RF-MBE growth. Reversing Ga polarity to N polarity could also be realized by nitridation of the deposited Al layers. These results provided a comprehensive understanding of the effects of surface stoichiometry, growth temperature and N source species (ammonia or N plasma) on GaN polarity. It was concluded that GaN tended to grow with Ga polarity which was kinetically favorable on thermally cleaned sapphire substrates and Al-covered surfaces, the polarity conversion of GaN by TMAI preflow, AlN intermediate layer or Al insertion layers relied on the fact that they provided an Al platform on which the subsequent epilayer prefers to grow with Ga polarity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metalorganic vapor phase epitaxy; Molecular beam epitaxy; GaN; Polarity

1. Introduction

One of the main characteristics of GaN is its polarity due to absence of symmetry center in the [0001] direction. The morphologies and properties of the films grown with Ga polarity and N polarity are quite different because of the different growth mechanisms predominant on the two polar surfaces [1,2]. The large piezoelectric and spontaneous polarization fields existing in nitride devices allow a significant tailoring of the carrier dynamics and optical properties. These effects can further be used, for instance, to generate two-dimensional carriers gases without modulation doping, and polarization enhanced Schottky barriers [3]. Theoretical calculation predicted that the polarity inversion domain boundaries (IDBs) would not affect the near band gap luminescence due to the absence of midgap electronic states, and it was very recently observed that the photoluminescence of IDBs was one order magnitude higher than that of bulk GaN [4]. To explore fully the

potential functions and applications of III-nitrides, it is necessary to understand and play with polarities.

Due to these interesting important features, intensive research works have been conducted on the growth behaviors of GaN with different polarities. Many factors were reported to influence the epilayer polarities, such as growth methods, buffer layer types, buffer layer temperature, substrate nitridation, surface stoichiometry, growth rate and so on [5–12]. So far, the related mechanisms are not understood well. The effects of polarity on GaN growth behaviors and properties, as well as the factors controlling the polarity selection process must be investigated in order to provide the knowledge necessary for further improvement of film crystal quality, and device performances.

Recently, we demonstrated polarity-controlled MOVPE growth of GaN by using trimethyl-aluminum (TMAI) preflow [2], and developed a ‘three-step growth method’ based on the polarity-control [6]. In this paper, we present our extensive studies on the polarity selection processes of GaN grown sapphire substrate by MOVPE and RF-MBE. The related mechanisms for polarity manipulation both in MOVPE and MBE growth are discussed based on the ‘two monolayers of Al’ model. Realization of polarity manipulation is the first important

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step toward exploring the super-functional optoelectronic devices by utilizing the polarization effects of III-nitrides.

2. Experimental

MOVPE growth of GaN was conducted at a chamber pressure of 200 torr [2]. The substrate was first thermally cleaned in H_2 ambient at 1100 °C for 10 min and then nitrided in the ammonia gas flow of 1500 sccm for 90 s. Prior to the deposition of a GaN buffer layer on the nitridated sapphire substrate, a TMAI preflow was introduced to cover the surface with at least two monolayers of Al at 550 °C, required to reverse the film polarity. Then, a 20-nm-thick GaN buffer layer and 2.5- μ m-thick GaN epilayer were grown on nitrided sapphire substrate at 550 and 1080 °C, respectively.

RF-MBE growth of GaN was carried out in a system with attached coaxial ion collision impact scattering spectroscopy (CAICISS) system. Active N was supplied from Applied EPI Uni-bulb RF plasma cell. To investigate the polarity selection process and polarity conversion mechanisms of GaN, Al insertion layers and AlN intermediate layers were used to manipulate the polarity. The detailed growth process can be seen in Xu et al. [7].

Polarities of GaN films were characterized by using RHEED and CAICISS. The polarity of GaN as well as the Ga/N polarity ratio was determined by comparing the experimental spectra and the theoretically simulated ones. The simulated CAICISS spectra with different N/Ga polarity percentages are shown in Fig. 1. The polar angle is defined as the one between incident ion beam and sample surface.

3. Results and discussions

3.1. Polarity manipulated growth of GaN by MOVPE

The CAICISS spectra of the samples grown without and with the TMAI preflow supplied for 2 s, 5 s, and 10 s prior to the low temperature buffer layer deposition are shown in Fig. 2a–d, respectively. GaN epilayer polarity can be identified by comparison of the measured spectra with the simulated spectra. It is shown that GaN films grown on the nitrided sapphire without TMAI preflow have N polarity, whereas GaN films grown using a TMAI preflow above 5 s possess Ga polarity. The sample with 2-s TMAI preflow time was mainly N-polar and a few-percentage of Ga-polar, i.e. mixed polarities. Anyway, it was found that TMAI flow prior to buffer layer deposition could dramatically convert the film from N polarity to Ga polarity.

Surface morphologies of the samples grown with different TMAI preflow time are shown in Fig. 3. The surface of GaN film with 2-s TMAI preflow showed

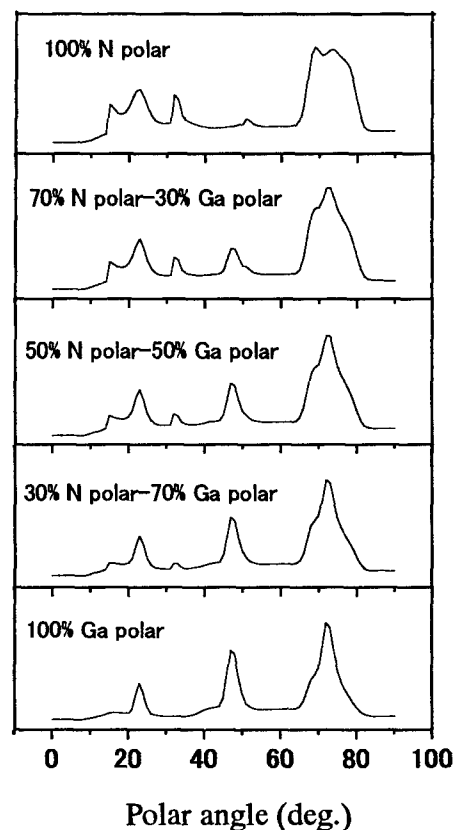


Fig. 1. Simulated CAICISS spectra of GaN with different Ga polar and N polar percentage. The spectra are Ga signal intensity dependence on the incident angle of He ion in $GaN_{[11\bar{2}0]}$ azimuth, the accelerated voltage is 2 kV, penetration depth is 10 Å.

still the hexagonal facets likewise the sample without TMAI preflow (0 s). However, the morphology of GaN films with TMAI preflow exceeding 5 s was dramatically changed into a flat surface.

The correlation of the TMAI preflow time and the resulting Al layer thickness is crucial to understand above experiment results. We have grown AlN by the MBE method. With very good reproducibility, after 400 cycles of growth at 1100 °C with the TMAI supply time of 2 s and a flow rate of 5 μ mol/min, cross-sectional field-emission scanning electron microscopy (FE-SEM) measurement showed that AlN layer thickness was approximately 90–105 nm. Since one monolayer of AlN is 0.2489 nm, 2-s TMAI supply with a flow rate of 5 μ mol/min corresponded to a monolayer AlN growth. In Fig. 3, Al layer thickness formed by 5-s TMAI preflow in a flow rate of 5 μ mol/min was estimated approximately at 2–2.5 monolayers. The polarity inversion structure was schematically shown in Fig. 4. We termed it as a model of ‘two monolayers of Al’. From the point of view of structure, two monolayers of Al are necessary and also sufficient to complete the conversion from N polarity to Ga polarity. The kinetic process of

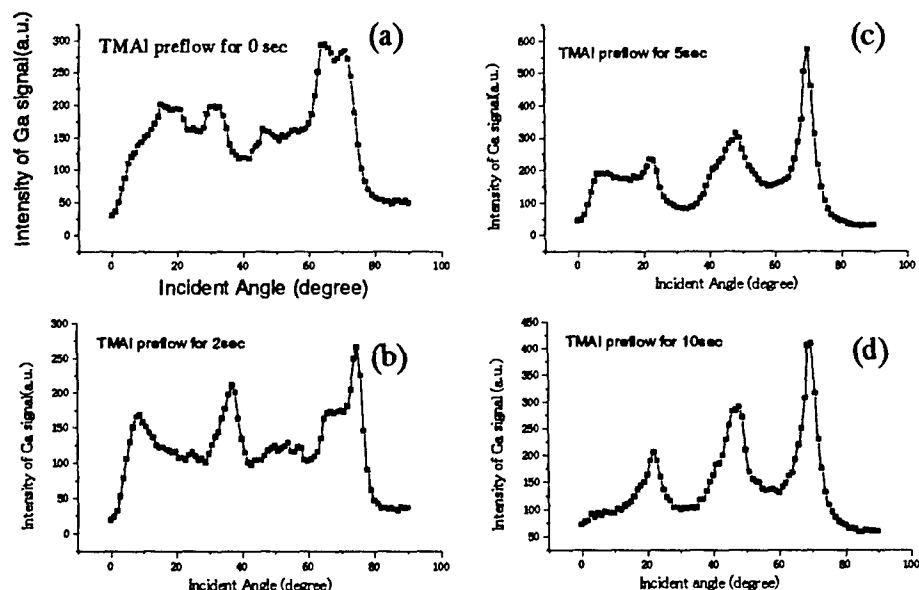


Fig. 2. CAICISS spectra of MOVPE grown GaN with different TMAI preflow times. Ga signal intensity dependence on the incident angle of He^+ , were recorded in $\text{GaN}_{[11\bar{2}0]}$ azimuth: (a) grown without TMAI preflow, N polarity; (b) with TMAI preflow of 2 s, mixed polarity; (c) TMAI preflow of 5 s, Ga polarity; and (d) TMAI preflow of 10 s, Ga polarity.

GaN polarity selection with Al insertion layers will be discussed in Section 3.3.4.

3.2. A new three-step method MOVPE growth for high-quality GaN epilayers based on polarity manipulation

A new three-step method has been developed to grow high-quality GaN epilayers based on polarity manipulation. The first step consists of substrate nitridation and growth of a thin AlN layer by the migration enhanced epitaxy method. Up to date, a number of experimental studies have been conducted to understand the nitridation processes. AlN could be formed on sapphire sub-

strate during nitridation, with the thickness of a nanometer scale depending on temperature and N sources. This will greatly improve the alignment of GaN or AlN crystal axis orientation on sapphire substrate, and decrease the relative rotations and tilts of crystal axis inside the nucleation layer. The thin, MBE-grown AlN layer was expected to inherit the sapphire substrate crystallinity and extend the high crystallinity from the nitridated sapphire substrate into the GaN layer.

Afterwards, the TMAI preflow and buffer layer were introduced to solve cracking and improve the surface morphology; this is the second step. TMAI was intentionally introduced to reverse the N polarity of AlN to

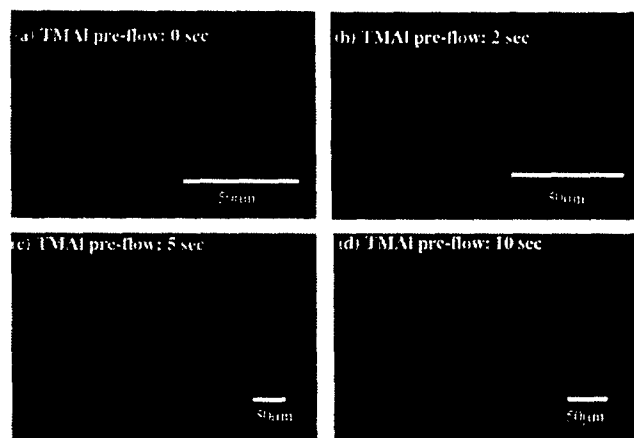


Fig. 3. Nomarski optical photographs of GaN films grown for different TMAI preflow times: (a) 0 s, (b) 2 s, (c) 5 s and (d) 10 s. The surface morphology of GaN films was changed into a flat surface by TMAI preflow periods exceeding 5 s.

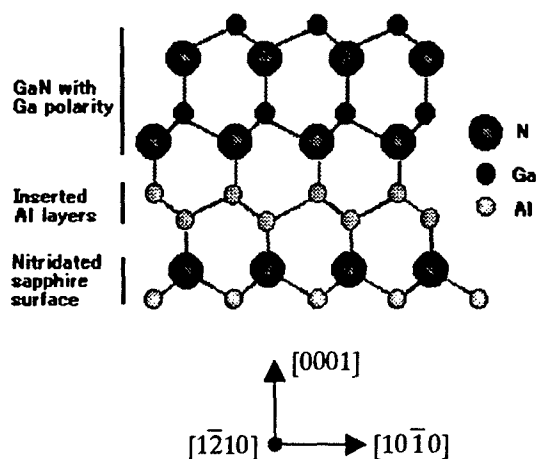


Fig. 4. A schematic model to illustrate the effect of TMAI preflow on GaN polarity.

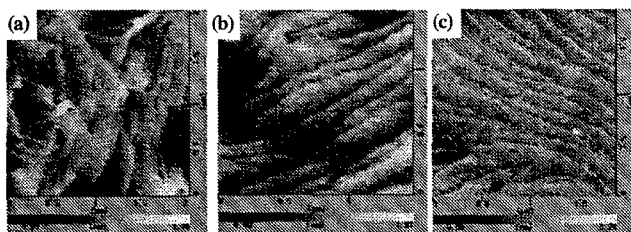


Fig. 5. AFM images of Ga polar epilayers grown with three different methods: (a) with conventional two steps, (b) with nitridation and TMAI preflow, and (c) grown with the three-step method.

the Ga polarity of GaN. The GaN buffer layer thickness was 20 nm.

The third step is epilayer growth at high temperature of 1080 °C. The ramping process from buffer deposition temperature to epitaxial temperature was executed in two steps, first with lower ramping rate below 900 °C, and higher ramping rate from 900 to 1080 °C.

The detailed mechanisms about the three-step growth, have been discussed in Yoshikawa and Takahashi [6]. As a comparison with the other growth methods, we show typical AFM images of GaN grown under the identical conditions but different methods in Fig. 5. Fig. 5a shows the sample grown by the conventional two-step method. The dark points correspond to the threading dislocations with a screw-type Burgers vector (pure screw or mixed), they reveal higher degree of relative tilts among the column structures. After applying nitridation to the sapphire substrate, the alignment of GaN columns on the substrate was improved, as shown in Fig. 5b, resulting in lower density of dark points. The Ga polar growth of this sample was realized by introducing TMAI preflow before low-temperature buffer layer deposition. Fig. 5c is the typical morphology of the GaN epilayer grown by the three-step method. Long growth steps without termination was observed, indicating a significant improvement to epilayer quality.

3.3. GaN polarity selection process and polarity manipulation in RF-MBE growth

3.3.1. Polarity of GaN grown on sapphire substrate

CAICISS spectra of GaN grown by RF-MBE on nitridated and non-nitridated sapphire substrates are shown in Fig. 6a,b. By comparing with the simulated results, we knew the film grown on extensively nitridated sapphire substrate was not 100% N polarity, but the estimated Ga polarity was below 5%; while the GaN epilayer grown on non-nitridated sapphire substrate was of well-defined Ga polarity. This result showed that, even the chemical activity of N supplied from RF plasma was very high, Ga polarity was favorable on the thermally-cleaned sapphire surface regardless of source supply order. Therefore, we could not simply refer RF-MBE grown GaN as N polarity.

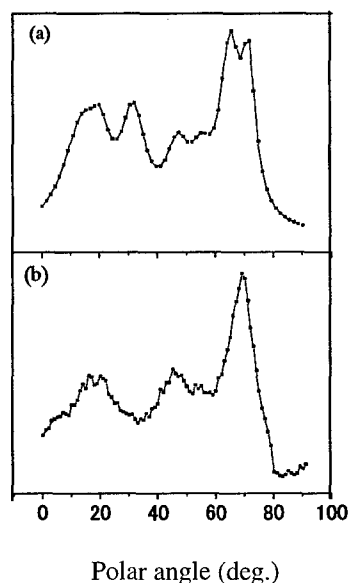


Fig. 6. CAICISS spectra of GaN grown by RF-MBE: (a) on extensively nitridated sapphire substrate; and (b) on non-nitridated sapphire substrate.

The thermally-cleaned sapphire substrate was usually terminated by Al in an ultra-high vacuum. In following, we investigated the effect of Al deposition on GaN polarities.

3.3.2. GaN polarity manipulation by Al insertion layer during RF-MBE growth

Fig. 7a shows the CAICISS spectrum of the GaN film which was grown on nitridated sapphire substrate but with 1-ML Al insertion during the epilayer growth. The signal is very complicated at a low angle. This may

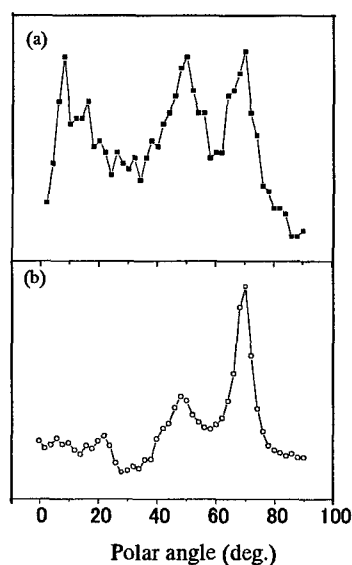


Fig. 7. CAICISS spectra of GaN: (a) 1-ML Al deposition during epitaxy; (b) 2-ML Al deposition for two times during epilayer growth.

be caused by the excess Ga coverage on the real surface. According to the peak shape from 60 to 80° in Fig. 7a, it was found the film was mixed-polarity, and the spectrum was close to the simulated one assuming 30% Ga polarity. For the sample grown with 2-ML Al deposition, the measured CAICISS spectrum was similar to Fig. 7a, but the Ga polarity percentage increased to approximately 70%. Following this, we tried the 2-ML Al deposition two times during the epitaxy. After 20-nm GaN growth on the first 2 ML of Al, the second deposition of 2-ML Al was done. The corresponding CAICISS spectrum is shown in Fig. 7b, it is clear that polarity of the epilayer was completely changed to the Ga one. Thus it has been confirmed that 2-ML Al coverage is necessary and also enough to reverse N polarity to Ga polarity. Logically, if 2 ML is not enough, the polarity will not be changed regardless of the deposition times. The yield of approximately 30% Ga polarity by 1-ML Al deposition is thought due to 2-ML Al islands formation. The yield of approximately 70% Ga polarity was attributed to the fact that the surface was not fully covered by 2-ML Al uniformly even the mean thickness of deposited Al layer was 2 ML.

We have also tried to reverse Ga polarity to N polarity by using Al insertion layer. It was shown that a much thicker Al layer and much stronger N plasma are necessary to complete the polarity conversion. Thus, 80% N polarity was yielded after 5-min nitridation to the 30-ML-thick Al layer with a N plasma condition of 500-W RF-power and 1.2 sccm N₂ flow rate. Evidently, the selection of N polarity on the surface featured with metal-like bonds was kinetically unfavorable.

3.3.3. RF-MBE growth investigation on GaN polarity inversion mechanism by high-temperature deposited AlN intermediate layer

In the third group experiment, GaN polarity selection on the AlN intermediated layer was investigated. The N-polarity GaN epilayer was grown at 820 °C with N plasma condition of 300-W RF-power and 0.8 sccm N₂ flow rate, corresponding GaN growth rate was 0.7 μm/h. Under this N plasma condition, a Ga flux as high as 2.5 A/s was needed to realize the pseudo-two-dimensional growth and this was also the upper limit for the Ga flux to avoid the Ga droplet. The AlN intermediate layer was grown by different methods. As stated above, the Al flux was fixed at 0.5 A/s for all experiments in this paper. We could switch GaN growth to AlN intermediate layer growth by simply closing the Ga shutter and open the Al shutter while keeping the N plasma condition the same. Accordingly, AlN was grown under the N-rich condition by this method. The CAICISS spectrum of GaN with a 20-nm-thick AlN intermediate layer grown under the N-rich condition is shown in Fig. 8a; it is a well-defined N-polarity spectrum. In situ

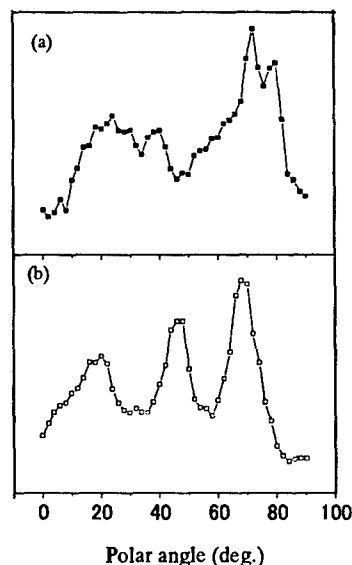


Fig. 8. CAICISS spectra of GaN: (a) GaN grown on AlN without N shutter modulation, i.e. under N-rich condition; (b) GaN grown on AlN with N shutter modulation.

RHEED monitoring confirmed that 20 nm of AlN can completely cover the GaN surface under the above growth condition. This result shows that the AlN intermediate layer grown under a N-rich condition will not change the polarity of the GaN epilayer.

Therefore, it has been found that the high-temperature deposited AlN layer itself could not convert N polarity GaN to Ga polarity. The surface stoichiometry of AlN during the growth is a critical point.

As a further investigation, even though both Al and N flux are kept the same as stated above, if the N shutter is modulated during AlN growth while the Al shutter is kept open, the Al/N ratio is adjusted to above unity. The polarity of the GaN epilayer grown under this condition could be perfectly changed to Ga polarity, as shown in Fig. 8b. In this growth method, the N shutter operation was modulated by 4 s open and 6 s close. The 6-s close of the N shutter allowed approximately 1.1 ML of Al deposition. In order to investigate why the Al/N ratio affects the polarity of GaN grown latter on, we examined the effect of AlN surface stoichiometry on GaN polarity. In the case that the AlN intermediate layer was grown under the same nitrogen-rich condition mentioned above, we did excess Al deposition before starting GaN growth on AlN at 820 °C. The Al deposition time was 12 s, corresponding to 2.2-ML coverage. The resulting GaN epilayer was proven to be Ga-polarity. The experimental results suggest that excess Al coverage on the AlN intermediate layer was crucial to reverse N polarity to Ga polarity by the AlN high-temperature intermediate layer.

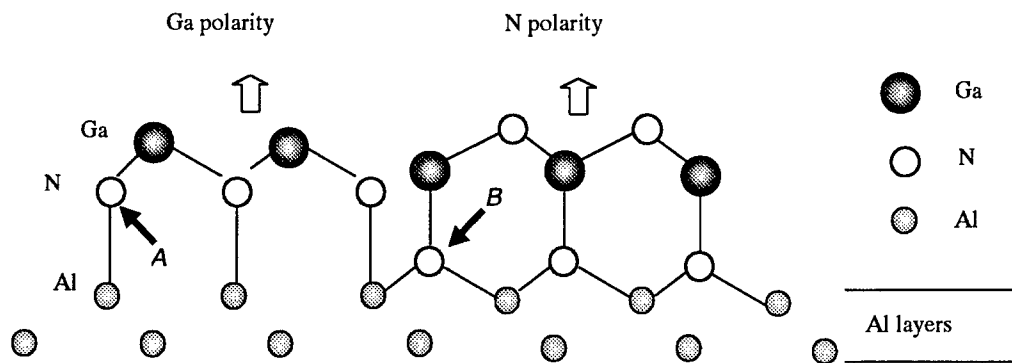


Fig. 9. Polarity selection process of GaN on the Al layer.

3.3.4. Kinetic process of GaN polarity selection on the Al layer

The GaN polarity selection process is schematically shown in Fig. 9. Since bonding energy between Al and N is higher than that between Ga and N, the polarity of GaN grown on the Al covered surface depends on bonding configuration among Al and N when Ga and N species arrive at the surface. If the N atom takes position A, Ga polarity occurs; if the N atoms take position B, N polarity occurs. STM characterization and theoretical calculation showed that Ga atoms in the GaN surface would form metallic bonds which were only slightly weaker than those formed in bulk Ga, coherently, we think the Al adlayer on the GaN surface may form much stronger metallic bonds than Ga atoms. For N atoms entering position B, it needs the cooperation among three Al atoms, therefore, N polarity is kinetically unfavorable on the Al covered surface. However, due to the high ionicity of III-nitrides, the growing epilayer tends to keep its polarity. To reverse Ga polar to N polar, much thicker Al-layer coverage and stronger N-plasma irradiation are necessary, which will be reported later.

4. Conclusions

Polarity manipulation of GaN on sapphire substrates both in MOVPE and MBE growth has been demonstrated. Polarity selection processes of GaN on nitrided, non-nitrided sapphire substrates, Al layers, and AlN intermediate layers were investigated. Results showed that, Ga polarity was kinetically favorable on thermally cleaned sapphire substrates and Al covered surfaces. Polarity conversion from N polarity to Ga polarity could be seen by Al insertion layers, and vice versa. GaN polarity reversing mechanism by AlN was also clarified. It is suggested that the polarity conversion of GaN by AlN or Al relies on the fact that they provide an Al

platform on which the subsequent epilayer preferred to grow with Ga polarity.

Acknowledgments

This work was partly supported by the 'Research for the Future Program', Japan Society for the Promotion of Science (JSPS-RFTF 96R16201) and the Grants-in-Aid for Scientific Research (B) #13450121, Japan Society for the Promotion of Science.

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